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Decontamination of Mild Steel Surfaces Containing Medium and High-Fired PuO_2

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ABSTRACT

Decontamination of surfaces contaminated with fission products and/or non-fired actinide oxides is generally accomplished chemically with chelating agents that have high stability constants for solubilization and removal of the contaminants. The effectiveness of the removal of soluble fission products and non-fired actinide oxides is determined by the ability of the decontamination agent to solubilize the contaminants and not dissolve the contaminated surface material. For decontamination of stainless steel, plastic, concrete, and other materials that are impervious to most decontamination agents, the most harsh decontamination agents, including acid solutions, can be used to remove contaminants. However, if the contaminants are refractory oxides, such as medium-fired or high-fired PuO_2 and the surface is easily attacked by harsh decontamination agents, then the decontamination effort becomes much more difficult.

With medium of high-fired PuO_2, common decontamination agents are ineffective in solubilizing and removing the Pu contaminant from a mild steel surface. When Pu is heated to high temperatures three forms of PuO_2 can result; non-fired or low-fired PuO_2 at <200°C, medium-fired PuO_2 at 450-650°C, and high-fired PuO_2 at >800°C. Common decontamination agents can be effective for solubilizing and complexing non-fired or low-fired PuO_2 but will be totally ineffectual for solubilizing and complexing medium-fired and high-fired PuO_2. Attempts to decontaminate with HNO_3-HF solution will result in dissolving the mild-steel materials. The only complexing agent that has the ability to break the Pu-O bond is the fluoride ion heated above 40°C in an acid solution.

To decontaminate medium and high-fired PuO_2, inhibited fluorides can break the Pu-O bond, solubilize and complex the dissolved Pu and only slowly attack a mild-steel surface. The use of fluoboric acid heated in mild acid solutions was found to be an effective inhibited fluoride for solubilizing and complexing all forms of PuO_2 for decontamination of mild-steel surfaces. The boron atom in fluoboric acid (HBF_4) forms a strong complex with the fluoride ion that allows solubilization of PuO_2 and inhibits the dissolution of materials, including mild-steel components. The development of this decontamination methodology is presented in this paper.

INTRODUCTION

Surfaces contaminated with PuO_2 are typically found in gloveboxes and containment structures in controlled areas in nuclear facilities at Los Alamos National Laboratory (LANL). Decontamination of surfaces contaminated with PuO_2 has been accomplished by a number of methodologies that include chemical decontamination with chelating or complexing agents, strippable foams or paints, electrochemical techniques, harsh acids, and removal of Pu as the volatile hexafluoride. All of these methods assume that the PuO_2 is easily soluble, labile, and present on highly refractory surfaces. However, decontamination of PuO_2 from mild steel

surfaces poses a significantly more challenging problem when the PuO_2 has been forced into cracks, imperfections, and grain boundaries in the metal. An important factor in establishing a method for decontamination of a non-refractory surface such as mild steel is whether the PuO_2 is in a form that is non-fired, medium-fired, or high-fired. PuO_2 that is non-fired or low-fired (<200°C) can be decontaminated with common decon agents and chemical complexants such as citrate, ethylenediaminetetraacetic acid (EDTA), or diethylenetriaminepentaacetic acid (DTPA), but medium-fired PuO_2 (450-650°C) or high-fired PuO_2 (>650°C) requires acids containing relatively concentrated nitric acid with strong oxidants that severely attack the mild steel surface during the decon process. A great number of potential decon compounds were tested to determine their potential to solubilize medium-fired PuO_2 and eventually to determine their effectiveness as decon agents for all forms of PuO_2. It was found that to chemically decon mild steel surfaces from a mixture of non or low-fired, medium, or high-fired PuO_2 that inhibited fluoride compounds were successful in the presence of dilute nitric, hydrobromic, or hydrochloric acids.

EXPERIMENTAL

To establish an effective chemical means to solubilize medium-fired PuO_2 (450 - 650°C), a series of experiments were conducted to determine an effective complexant that solubilized the PuO_2 and removed it from a mild steel surface without severely attacking the mild steel matrix. The chemicals and chemical mixtures tested are given in Table I, Table II, and Table III. Hydrofluoric acid was found to be the most effective solution for solubilizing medium-fired PuO_2 but it also rapidly dissolved the mild steel. Two compounds that were tested and found to be effective in dissolving medium-fired PuO_2 and not severely attack mild steel were fluoboric acid (HBF_4) and fluosilicic acid (H_2SiF_6). In each compound, the fluoride ion is strongly attached to a boron or silicon atom which inhibits the reactivity of the fluoride ion towards other compounds or materials containing atoms less attracted to the fluoride ion in an acid solution. Because of the inhibition of the reactivity of the fluoride ion in the presence of B or Si, these compounds were termed inhibited fluoride compounds or agents. In other words, the stability constant for the fluoride ion for Fe in mild steel was inhibited because of the greater stability constant for the fluoride ion with B or Si. Alternatively, the high stability constant for the fluoride ion for Pu was great enough to break the Pu-O bond (dissolve the PuO_2) and not dissolve the Fe in mild steel.

Table I

CONDITIONS TESTED TO SOLUBILIZE MEDIUM – FIRED PuO_2 AND DISSOLUTION TIMES

	Dissolution Matrix	Time to Dissolution
1.	9 N HBr	none
2.	2. 50% K_2CO_3 + 5 % HBF_4	ppt + gel formation
3.	.1 N EDTA + .1 M $Na_2S_2O_4$	none
4.	50% K_2CO_3 + 5 % HBF_4 + 5% NaOCl	ppt + gel formation
5.	2 N HNO_3 + 5% H_2PO_3F	>60 min
6.	2 N HNO_3 + .1 M Ce(IV)	60 min
7.	2 N HNO_3 + 5% HBF_4 + 3% H_3BO_3	30 min
8.	1 N HNO_3 + 5% H_2SiF_6	15 min
9.	1 N HNO_3 + 5% HBF_4	10 min
10.	2 N HBr + 5% HBF_4	5 min

**Conditions: Medium-fired PuO_2(~600°C), Heat with stirring at 80°C for up to 1 hour, Visual observations*

Table II

CONDITIONS TESTED TO SOLUBILIZE MEDIUM-FIRED PuO_2 AS A FUNCTION OF TEMPERATURE AND TIMES

	Dissolution Matrix	Temp	Time to Dissolution
1.	20% K_2CO_3 + 5% H_2SiF_6	80 °C	ppt + gel formation
2.	0.1 M EDTA + 1% $Na_2S_2O_4$	80 °C	none
3.	5% Sulfamic acid + 5% HBF_4	80 °C	>60 min
4.	2 N HNO_3 + 0.01 N Ce(IV) + 1% $KBrO_3$	80 °C	>60 min
5.	1 N HBr + 2% H_2SiF_6	80 °C	>60 min
6.	1 N HBr + 5% HBF_4	60 °C	>45 min
7.	2 N HBr + 5% HBF_4 +$Na_2S_2O_4$	80 °C	30 min
8.	1 N HBr + 2% HBF_4	80 °C	30 min
9.	1 N HNO_3 + 2% HBF_4	80 °C	25 min
10.	1 N HNO_3 + 2% H_2SiF_4	80 °C	20 min
11.	1 N HCl +5% HBF_4	60 °C	15 min
12.	1 N HNO_3 + 5% HBF_4	60 °C	10 min
13.	4 N HBr + 5% HBF_4	80 °C	5 min

Conditions: Medium-fired PuO_2 (~600 °C), Heat with stirring at 60 °C and 80°C for up 1 hr, Visual Observations

Table III

CONDITIONS TESTED TO SOLUBILIZE MEDIUM-FIRED Pu AND PERCENT DISSOLVED

Dissolution Matrix	% Dissolution
1. 2 N HNO_3 + 0.1 N HBr	<1%
2. 2 N HNO_3 + 0.1 N HBr + 1% Dithionite	<1%
3. 4 N HBr	<1%
4. 4 N HBr + 1% Dithionite ($Na_2S_2O_4$)	<1%
5. 10% Sulfamic Acid	<1%
6. 50% K_2CO_3 + 5% NaOCl + 1% NTA	<1%
7. 50% K_2CO_3 + 5% NaOCl + 1% H_2O_2	<1%
8. 2 N HNO_3 + 0.1 N HBr + 1% $KBrO_3$	~7%
9. 2 N HNO_3 + 5 drops 1.3 N HF	61%
10. 5% HBF_4	83%
11. 4 N HNO_3 + 0.01 N Ce(IV)	84%
12. 4 N HNO_3 + 0.1 N Ce(IV)	97%
13. 2 N HNO_3 + 5% H_2SiF_6	>99%
14. 2 N HNO_3 + 0.1 N HBr + 5% HBF_4	>99%
15. 2 N HNO_3 + 5% HBF_4	100%

The effectiveness of fluoboric and fluosilicic acid at different concentrations in 2M HNO_3 at 80°C is given in Table IV. Table V shows the effect of 1N, 2N, and 4N HNO_3 in 2%, 4%, and 8% HBF_4 and H_2SiF_6 at 60°C while TABLE VI gives the results for the same concentrations at 45°C.

Table IV

DECONTAMINATION WITH INHIBITED FLUORIDES AT 80°C

•Approximate time (in minutes) to dissolve nominal 10 mg medium-fired PuO_2 in 10 ml solution at 80°C

	Chemical Concentration in 2N HNO_3	Dissolution time (min)
	2%	5
HBF_4	4%	2
	8%	1.5
	2%	5
H_2SiF_6	4%	2
	8%	1.5

Table V

DECONTAMINATION WITH INHIBITED FLUORIDES AT 45°C

* Approximate time (in minutes) to dissolve nominal 10 mg medium-fired PuO_2 in 10 ml solution at 45°C

HBF_4	1N HNO_3	2 N HNO_3	4 N HNO_3
2%	>55	40	25
4%	-	20	17
8%	40	16	10

H_2SiF_6	1N HNO_3	2 N HNO_3	4 N HNO_3
2%	-	-	55
4%	-	-	45
8%	-	>30	30

Table VI

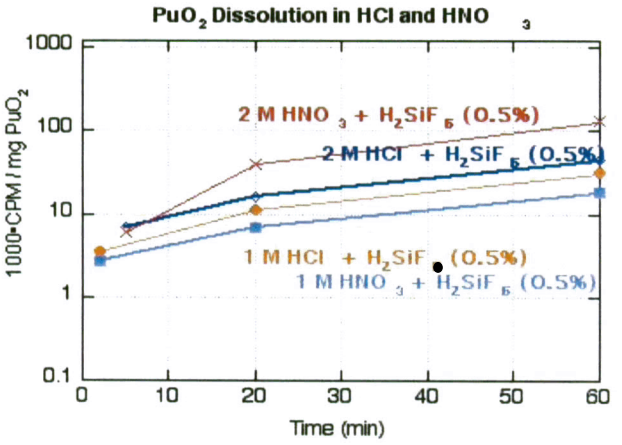
DECONTAMINATION WITH INHIBITED FLUORIDES AT 60°C

*Approximate time (in minutes) to dissolve nominal 10 mg medium-fired PuO_2 in 10 ml solution at 60°c

HBF_4	1N HNO_3	2 N HNO_3	4 N HNO_3
2%	25	11.5	7
4%	11	7	3.5
8%	6	4	2.5

H_2SiF_6	1N HNO_3	2 N HNO_3	4 N HNO_3
2%	>45	23	16
4%	25	12	9
8%	10	7	5

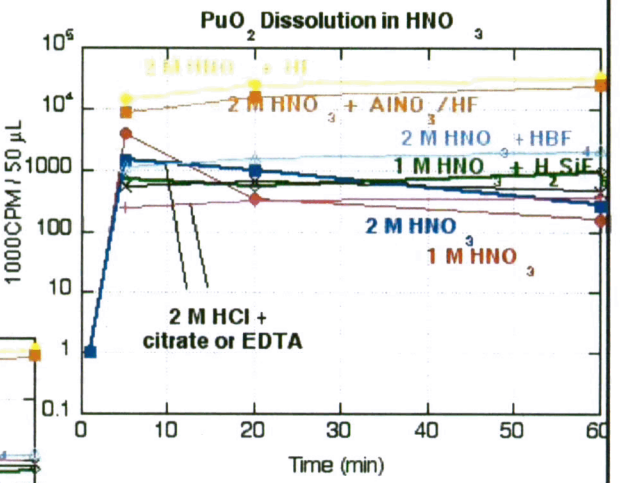
To determine the effectiveness of inhibited fluorides on the dissolution of PuO_2 in different acids, several experiments were conducted in different concentrations of HCl, HNO_3, HBF_4, and H_2SiF_6 as shown in Figures 1, 2a, and 2b, and 3. The enhancing effect of inhibited fluorides for dissolving medium-fired PuO_2 is shown in Figure 4. A comparison of different complexing agents versus HBF_4 and H_2SiF_6 is shown in Figure 5.

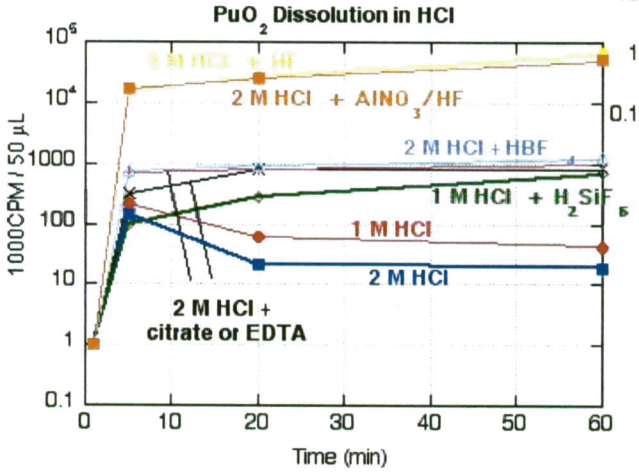


- Effect of acid concentration on PuO2 dissolution is small

Figure 1: Effect of Inhibited Fluoride on Dissolution of PuO_2

- Slow PuO_2 dissolution in pure HCl or HNO_3
- Addition of Fluoride increases dissolution kinetics of PuO_2 significantly





HBF_4 appears as good fluoride source to dissolve PuO_2

Figures 2a an 2b : Effect of Inhibited Fluoride on Dissolution of PuO_2

- HCl and HNO_3 very slowly dissolve PuO_2
- Addition of inhibited fluoride increases PuO_2 dissolution
- Effect of acid concentration on PuO_2 dissolution is small

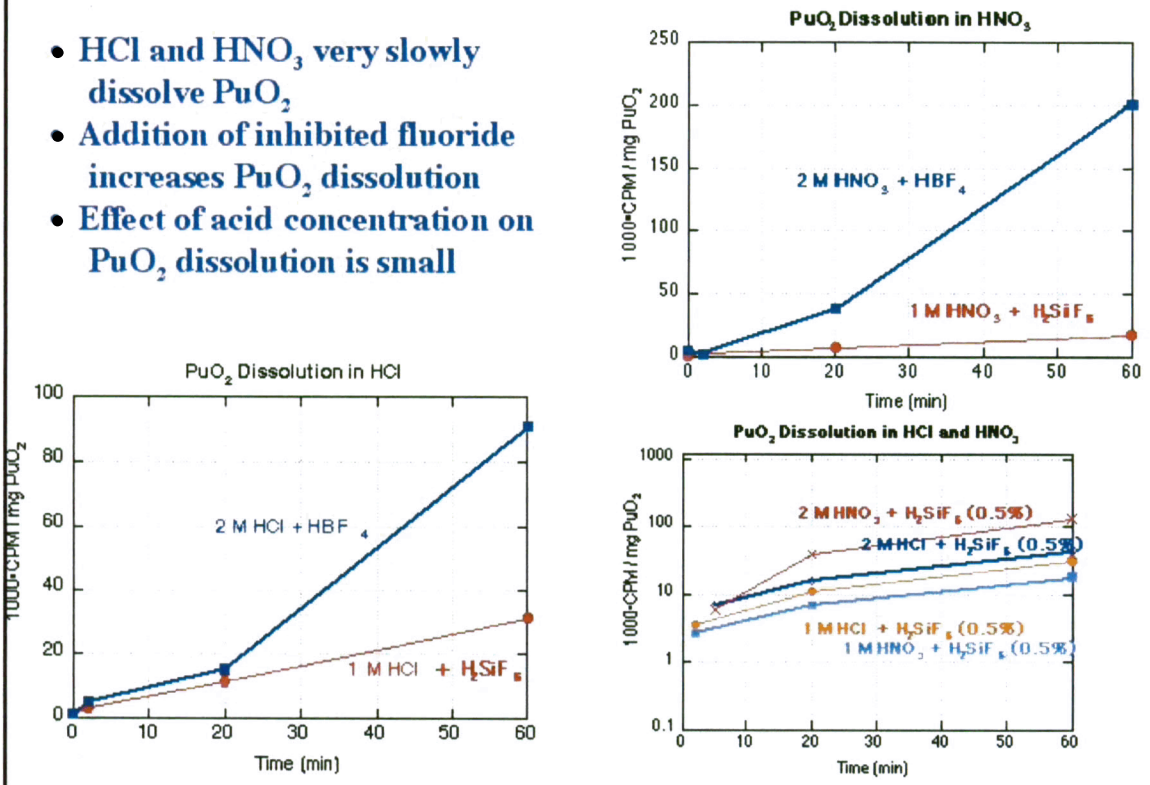
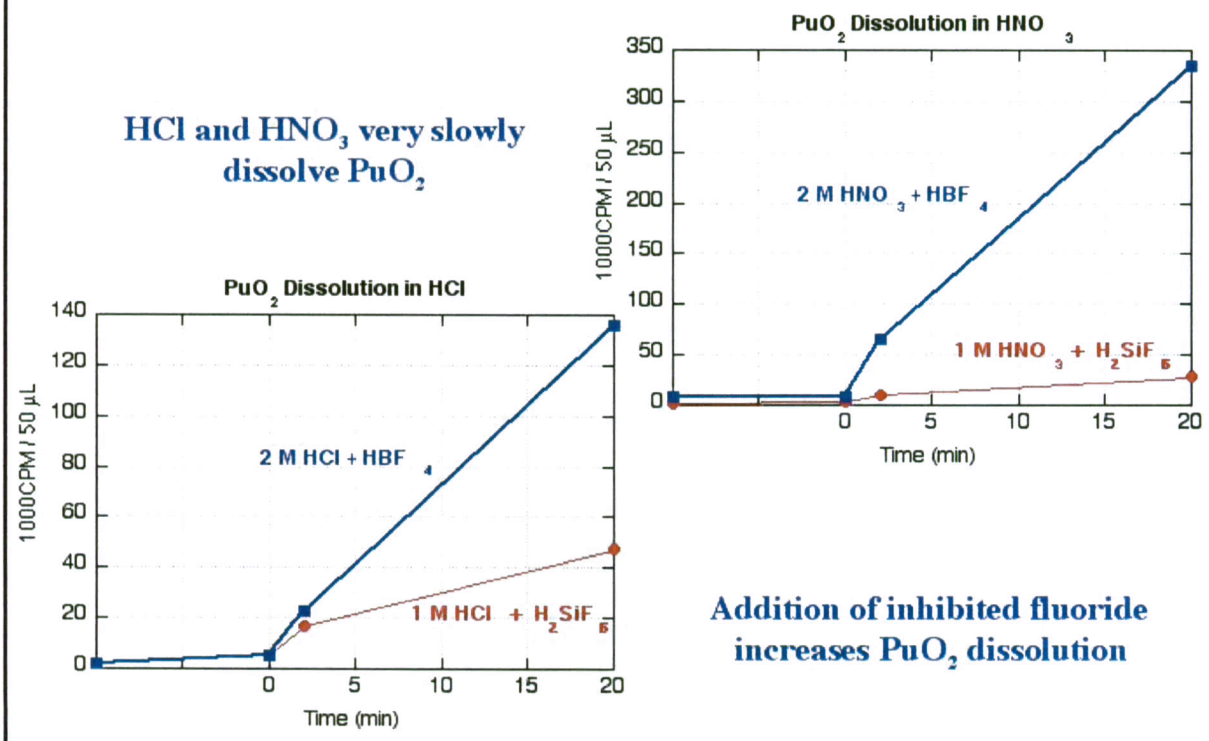


Figure 3: Effect of Inhibited Fluoride on Dissolution of PuO_2

HCl and HNO_3 very slowly dissolve PuO_2



Addition of inhibited fluoride increases PuO_2 dissolution

Figure 4: Effect of Inhibited Fluoride on Dissolution of PuO_2

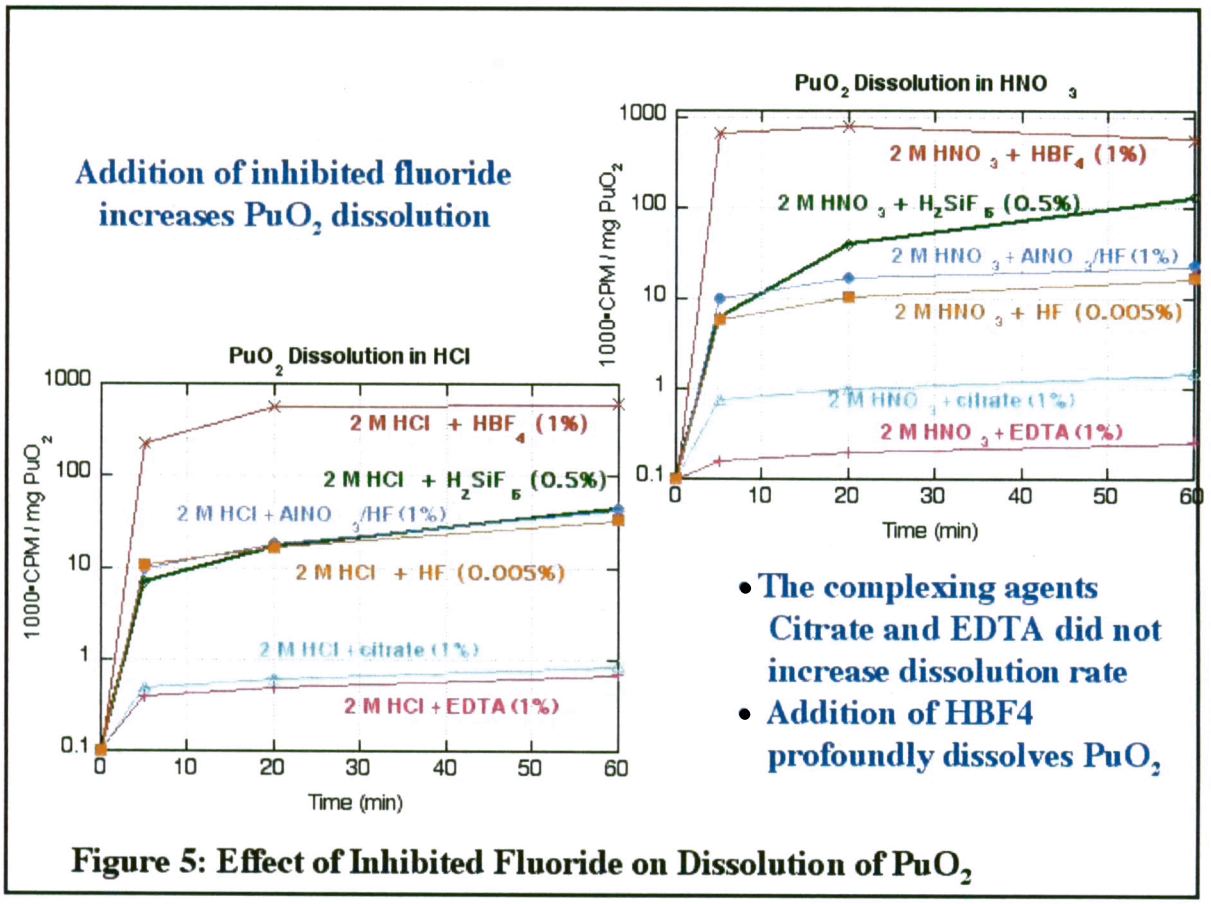
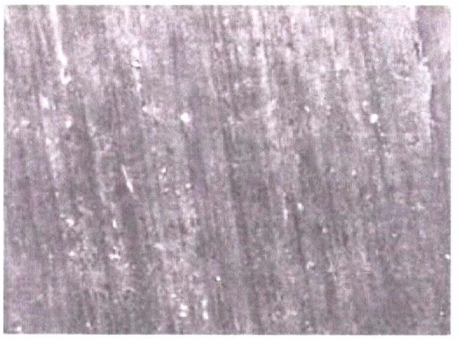


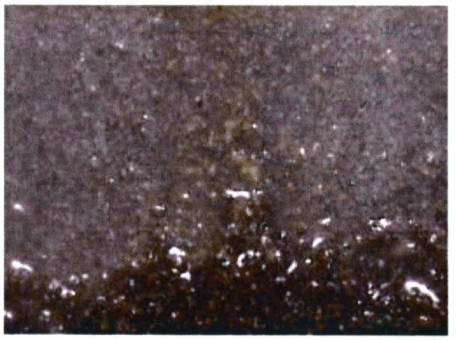
Figure 5: Effect of Inhibited Fluoride on Dissolution of PuO_2

The effect of acid solutions on mild steel coupons is shown in Figures 6 and 7.

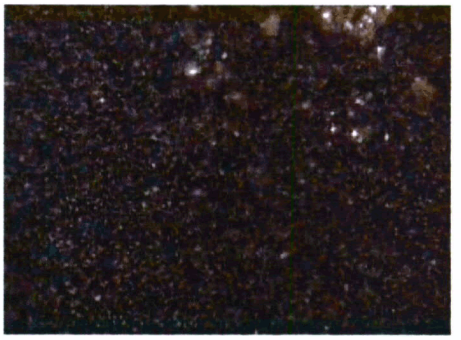


Steel surface before experiments with 1 M HCl

In solution for 2 min, 60 °C

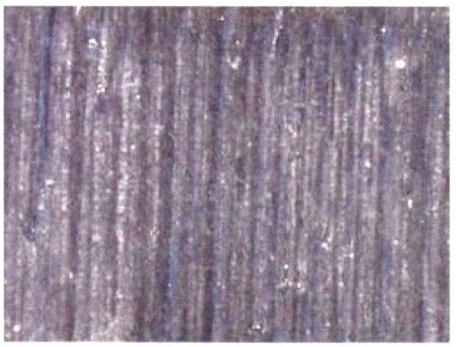


In 1 M HCl at RT, after weeks

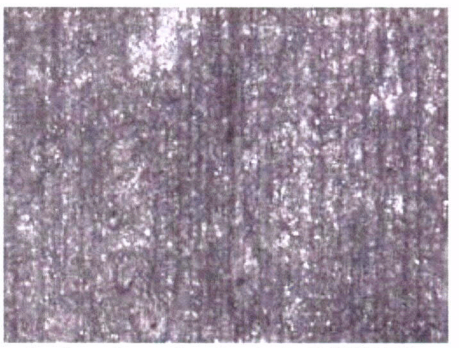


Steel above 1 M HCl solution, after weeks

Figure 6: Steel in Contact with 1 M HCl



Steel surface before experiments with 1 M H_3PO_4



Steel surface after 3 min in 1 M H_3PO_4

Steel surface after 12 min in 1 M H_3PO_4

Steel surface after 39 min in 1 M H_3PO_4

Figure 7: Steel in Contact with 1 M H_3PO_4

The photos in Figure 6 show that mild steel coupons exposed to 1M HCl at 60°C for 2 min has a minor effect on the surface. However, mild steel coupons in 1M HCl for longer periods (> 2-3 hours) severely corrode the surface and mild steel at HCl concentrations greater than 1M showed significant corrosion, especially for longer times.

The photos in Figure 7 show that 1M H_3PO_4 does not corrode the surface of mild steel as severely as 1M HCl. However, the use of H_3PO_4 as a base acid for inhibited fluorides has not been thoroughly investigated at this time. The importance of only superficially attacking the surface of mild steel coupons with the base acid is that the PuO_2 must be removed from the grain boundaries of the mild steel, but leaching too much Fe makes the separation of solubilized Pu and Fe much more difficult, especially in the presence of inhibited fluorides.

If the separation of Pu from Fe solubilized by HCl or HNO_3 in combination with inhibited fluoride is necessary, the solubilized Pu can be separated as a $PuO_2(IO_3)_2 \cdot H_2O$ precipitate in an acid solution by addition of KIO_4. The structure of the $PuO_2(IO_3)_2 \cdot H_2O$ molecule that is relatively insoluble is shown in Figure 8.

Consequently, to most effectively decontaminate multi-fired PuO_2 from mild steel surfaces, a low concentration of 1-2 M HCl or HNO_3 is preferable with a 1-2% inhibited fluoride solution at a temperature that will remove the PuO_2 within 5-10 min or less.

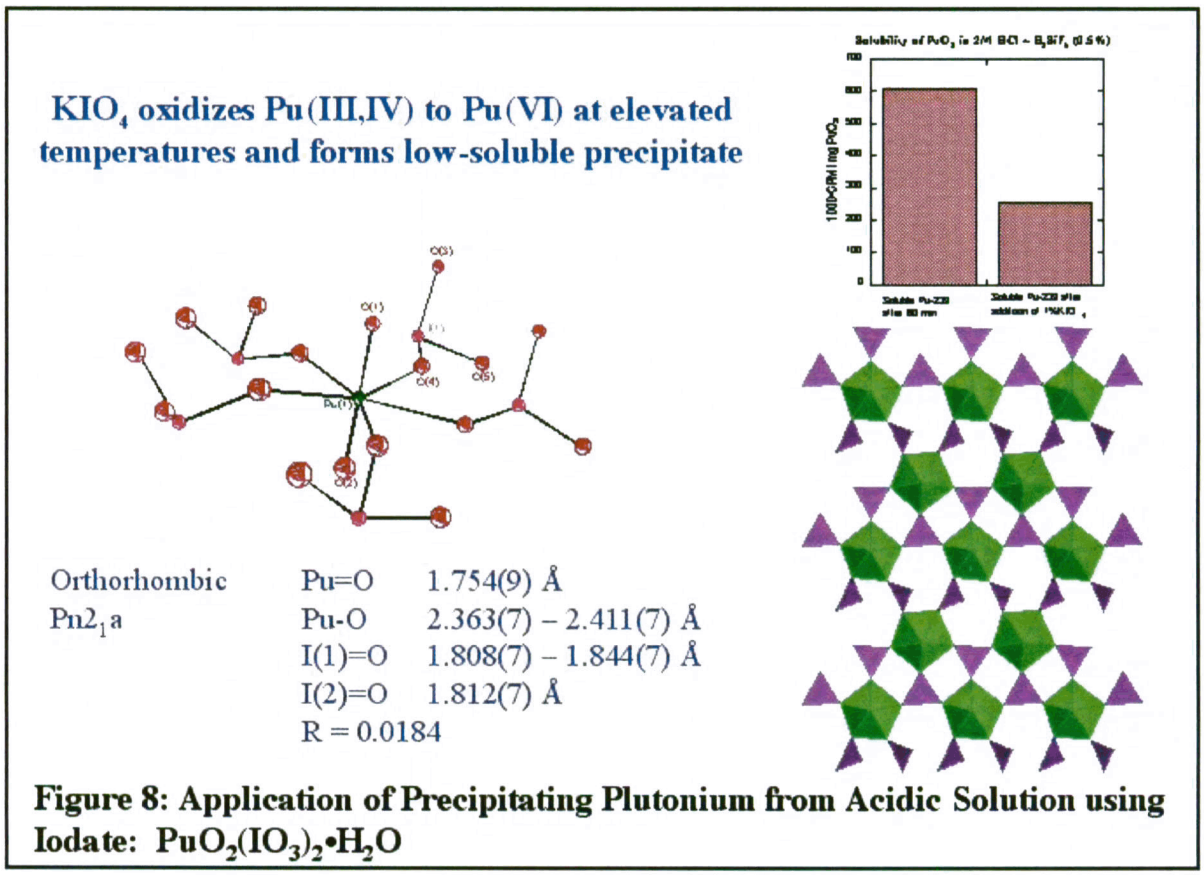


Figure 8: Application of Precipitating Plutonium from Acidic Solution using Iodate: $PuO_2(IO_3)_2 \cdot H_2O$

CONCLUSIONS

All forms of PuO_2 (non-fired, low-fired, medium-fired, and high-fired) were successfully removed from mild steel surfaces with inhibited fluorides in dilute solutions (1-2M) of HNO_3 and HCl. There was some attack of the mild steel surface by inhibited fluorides in 1-2M acid, but the attack was superficial compared to hydrofluoric acid solutions. We believe this is a straight-forward and effective method that is applicable to many other D&D situations, including decontamination of PuO_2 from soils or D&D of surfaces contaminated with multi-fired PuO_2 from a Radiological Dispersive Device (RDD).